ESTCP
Cost and Performance Report

(SI-0311)

Total Copper Analyzer for Rapid In Situ Characterization of Effluent Discharges

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ACRONYMS AND ABBREVIATIONS

$\mu g/L^{-1}$	micrograms per liter, same as parts per billion (ppb)
µm	micrometer, or one millionth of a meter
BMP	best management practices
CRADA	Cooperative Research and Development Agreement
CCC	criterion continuous concentration
CMC	criterion maximum concentration
Cu	copper
Cu-ISE	copper ion-selective electrode
$Cu(II)_{aq}$	aqueous free copper ion
CWA	Clean Water Act
DI	deionized (water)
DoD	Department of Defense
ECAM	Environmental Cost Analysis Methodology
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
gal/day^{-1}	gallons per day
GFAA	graphite furnace atomic absorption
ICP-MS	inductively coupled plasma mass spectrometry
$K	thousands of U.S. dollars
mV	millivolt (one thousandth of a volt)
mL/min^{-1}	milliliters per minute
NDCEE	National Defense Center for Environmental Excellence
NPDES	National Pollutant Discharge Elimination System
ONR	Office of Naval Research
psu	practical salinity units
PHNS	Pearl Harbor Naval Shipyard
ppb	parts per billion
PSNS	Puget Sound Naval Shipyard
QA/QC	quality assurance/quality control
R^2	correlation coefficient

SBWWTP	Schofield Barracks Waste Water Treatment Plant
SSC-SD	SPAWAR Systems Center-San Diego
S&H	Shipping and Handling
TCA	Total Copper Analyzer
WQC	water quality criteria

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Technical material contained in this report has been approved for public release.

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Copper (Cu) is a high-profile ubiquitous contaminant found in numerous point and nonpoint source effluents, including those generated by activities from the Department of Defense (DoD). Because Cu is highly toxic to larval organisms, the Environmental Protection Agency (EPA) considers this heavy metal a priority pollutant, and its discharge is under regulatory control (U.S. EPA, 1980, 1985). Water quality criteria (WQC) for dissolved Cu in receiving bodies of water includes a freshwater criterion maximum concentration (CMC), also known as acute value, of 13 micrograms per liter ($\mu g/L^{-1}$) or parts per billion (ppb), and a freshwater criterion continuous concentration (CCC), also referred to as chronic value, of 9 $\mu g/L^{-1}$. For saltwater, those criteria are a CMC of 4.8 $\mu g/L^{-1}$ and a CCC of 3.1 $\mu g/L^{-1}$ (U.S. EPA, 2003). While concentrations in ambient waters are regulated as the dissolved fraction (i.e., filtered through 0.45 µm pore-size), regulation of effluents is done on the total recoverable fraction (i.e., unfiltered, acidified to pH 2 and digested).

A rapid, in-place, characterization of total recoverable Cu in effluents can be accomplished by the Total Copper Analyzer (TCA) shown in Figure 1. This in-place characterization will allow for the rapid separation of the effluent between that in compliance and that in need of treatment, thus reducing the costs of operation, since the volume of water sent for treatment can be minimized. This characterization will also provide important information for the management of sources of Cu within the installation.

The demonstration and validation of the TCA is important because there is no other known instrument capable of measuring total recoverable Cu, either in situ or at near-real-time (i.e., within 5 minutes). Conventional characterization of effluents is performed off-site with laboratory tests, with the associated costs and turnaround time, often taking weeks for processing. As the TCA will provide a means to verify that the discharge is within permit requirements for Cu, in near-real-time and at the place of discharge, it will be a great asset for any regulated discharger, both private and public, including the DoD.

This demonstration and validation of the TCA under industrial situations supports its use as a management tool in most situations. Agreement with Cu concentrations measured with the accepted graphite furnace atomic absorption (GFAA) and inductively coupled plasma mass spectrometry (ICP-MS) technologies support the performance of the TCA in cases of saline waters with low organic matter content (i.e., discharges from dry docks). However, as the performance of the TCA did not meet the expectations under conditions of high organic matter (i.e., outfall of a wastewater treatment plant), the application of the TCA for regulatory purposes is not warranted.

1.2 OBJECTIVES OF THE DEMONSTRATION

The main objective of the demonstration is to validate the use of the TCA for continuous measurement of total recoverable Cu in industrial situations at full-scale. The TCA was deployed in three industrial settings and was allowed to operate continuously for more than a month in each case.

1.3 REGULATORY DRIVERS

Federal regulations that require the determination of total recoverable Cu concentration in effluents include the WQC (U.S. EPA, 2003), and the National Pollutant Discharge Elimination System (NPDES) program, which was developed under the Clean Water Act (CWA) to eliminate or reduce pollutant inputs to aquatic systems by imposing concentration limits on discharges.

1.4 DEMONSTRATION RESULTS

Total recoverable Cu measured in effluents by the TCA concurs with that measured using more traditional methods. This was demonstrated by the similitude in total Cu concentrations measured by the TCA to those measured by both GFAA and ICP-MS in grab samples taken from Puget Sound Naval Shipyard (PSNS) and Pearl Harbor Naval Shipyard (PHNS) at the time of the demonstration in each site.

The range of total recoverable Cu concentrations and its output rate make the TCA a significant discharge management tool. The dynamic range of the TCA measured under laboratory conditions is from 0.5 to 400 $\mu g/L^{-1}$ in deionized (DI) water and from 2 to 400 $\mu g/L^{-1}$ in artificial seawater with salinity 32 practical salinity units (psu). The lower limits in these ranges are considered the limits of detection. These ranges and limits of detection are considered relevant for industrial and regulatory purposes. The TCA has an accuracy of 99% with a precision better than ± 3 $\mu g/L^{-1}$ ($\pm 6.8\%$) at the 30 $\mu g/L^{-1}$ level. The TCA measurements are considered as near real-time as there is a lag of 5 minutes from intake to measurement of total Cu in the sample. But, as the TCA is a flow-through system, the continuous output of data can be adjusted down to few seconds, providing a stream of information for management of the discharge. However, there is a need for daily verification of the working status of the TCA.

Use of the TCA under extreme conditions of organic matter and in the presence of oxidizers is not warranted. In controlled laboratory conditions, the TCA had a decrease in sensitivity of 16% in the presence of 5 $\mu g/mL^{-1}$ humic acid. The effect of organic matter was observed in the demonstration at Schofield Barracks Waste Water Treatment Plant (SBWWTP). There the TCA measured Cu concentrations up to 29 $\mu g/L^{-1}$ larger that those measured by GFAA and ICP-MS. Our experience is that Cu measurements by the Cu ion-selective electrode (Cu-ISE) are affected by the presence of strong oxidants, such as hypochlorite (bleach).

1.5 STAKEHOLDER/END-USER ISSUES

The primary objective of this demonstration is to prove to the stakeholders the qualifications of the TCA. Parameters that are determined in the demonstration include the precision, accuracy and dynamic range of the total recoverable Cu measurements, the working-life expectancy, and the required maintenance schedule by the TCA. The results attest to the capability of the TCA for management of discharges in many cases. The results also indicate that there are instances where the TCA provides erroneous information, precluding its acceptance for regulatory purposes. Results from this demonstration are provided to stakeholders for any decision concerning the TCA.

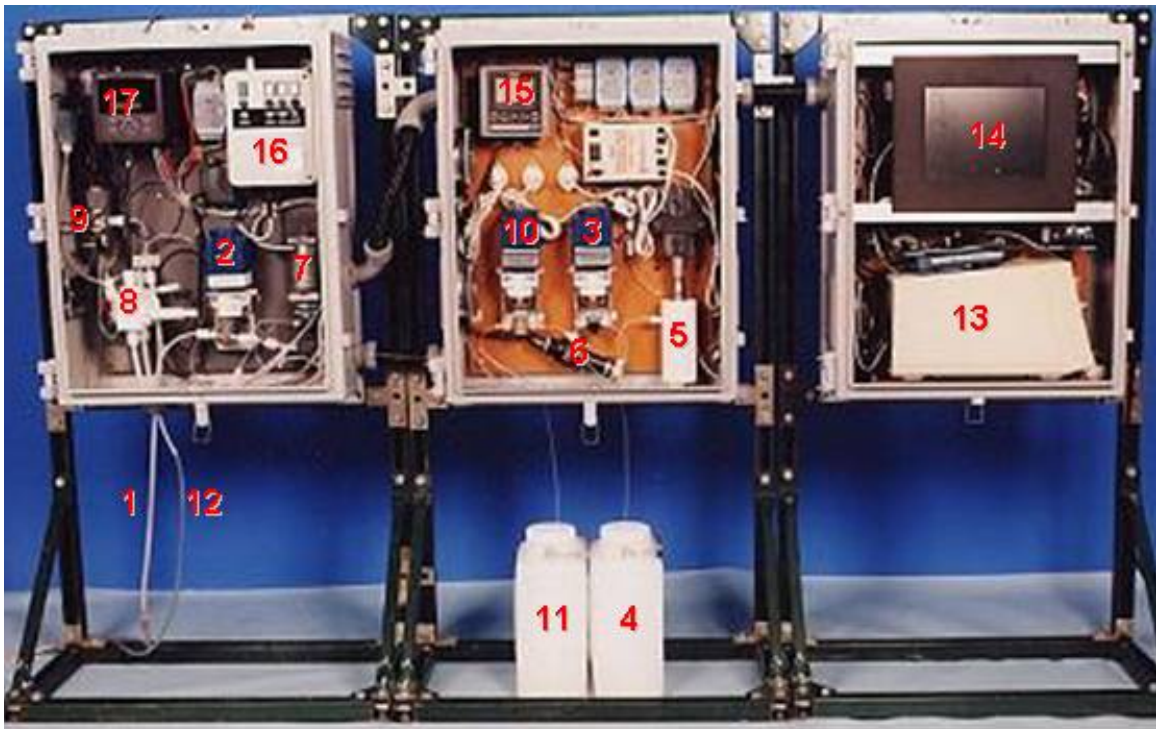

Figure 1. The Total Copper Analyzer Is the First Instrument Capable of Measuring Total Recoverable Copper in Effluents In Situ in Near-Real-Time and at Environmentally Relevant Concentrations.

Note: Major components are identified in Figure 1, with the first 12 following the sample path:

1 = Intake
2 = Recirculation pump
3 = Acidification pump
4 = Acid reservoir
5 = Ultrasonification probe
6 = Density probe
7 = Calibration pump
8 = Cu-ISE
9 = pH probe
10 = Neutralization pump
11 = Neutralizer reservoir
12 = Outlet
13 = Ultrasonification power supply
14 = Computer
15, 16, and 17 = power supplies and controls for probes

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2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

The TCA was designed to accomplish, in near-real-time, Method 3020A, approved by EPA for "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy" (U.S. EPA, 1992). In order to accomplish this goal, the TCA includes in-line automatic acidification, fast digestion of the effluent with an ultrasonic probe, and the use of a specialized jalpaite Cu-ISE, instead of GFAA, to measure the concentration of Cu. Due to the characteristics of the acidified and digested effluent, a substantial amount of the Cu will be present as aqueous free copper ions ($Cu(II)_{aq}$), which are detected by the Cu-ISE. The resulting measurement is equivalent to the total recoverable Cu concentration. The TCA could be used for management of industrial discharges, with either freshwater or saline water. However, use of the TCA in situations of high organic matter content or in the presence of strong oxidants (i.e., bleach) is not warranted.

2.2 PROCESS DESCRIPTION

The analysis consists of three processes—a chemical/physical treatment (i.e., acidification to pH 2 and digestion) of the sample, detection and reporting, and neutralization prior to discharging (Figure 2). In order to reduce contamination and to extend the working life of the TCA, most of the parts of the TCA that are in contact with the effluent are made of Teflon®. A continuous stream of effluent is pumped into the TCA at a constant rate (13.8 mL/min^{-1}). Total recoverable Cu is continuously measured and reported for the whole stream of effluent, but there is a lag of about 5 minutes from the time of intake to the actual measurement. The rate for reporting is controlled by the computer. For the demonstrations, a reporting rate of 30 seconds was used, providing 120 measurements per hour, but faster reporting rates can be used. The stream of effluent is first treated chemically by acidification to pH 2 with 5% nitric acid (0.25 mL/min^{-1}), then physically digested by ultrasonification. The digestate is then directed to the detection system, which includes a conductivity probe, Cu-ISE, reference electrode, and a pH electrode. The Cu-ISE and the high-volume, single-junction reference electrode measure a potential millivolt (mV) that is equivalent to the concentration of $Cu(II)_{aq}$. This potential, as well as temperature, pH, and conductivity are fed into a computer for calculation and reporting of the concentration of total recoverable Cu in the effluent. Finally, the sample is neutralized to pH 7 with 6% sodium bicarbonate (0.55 mL/min^{-1}) before the sample leaves the TCA.

The TCA was developed to include automatic calibrations of the Cu-ISE for the measurement of total recoverable Cu. This is done online by injection of a standard solution of known concentration with matched salinity to the effluent. Several (up to four) well constrained flow rates of this standard are injected for specific lapses of time (one hour) in order to generate the information for analysis by standard addition. The information is provided to the computer for verification of the total recoverable Cu measured in the effluent stream. In contrast, the conductivity probe and pH electrode require manual calibration with appropriate buffers at the moment of installation of the TCA in the discharge effluent, or for laboratory experiments.

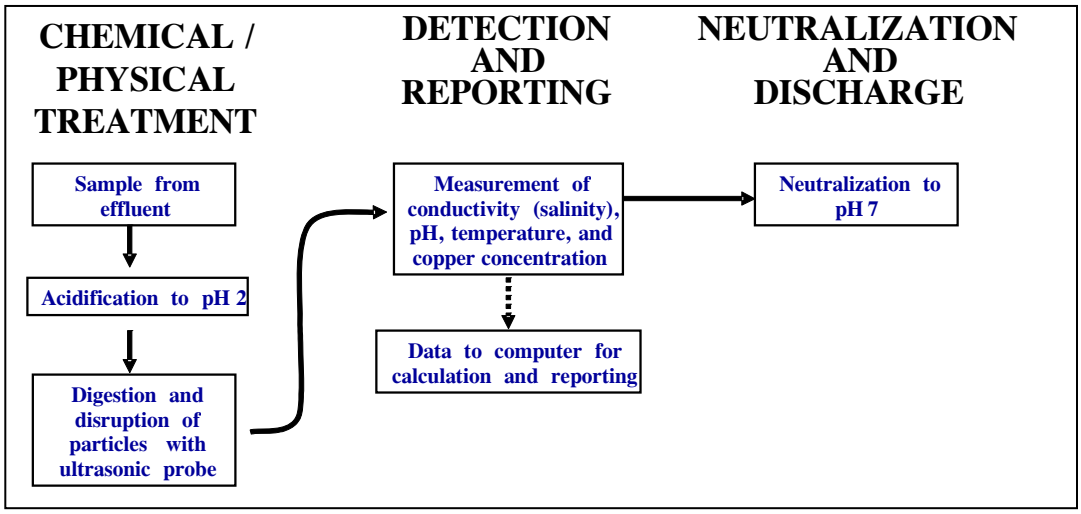

Figure 2. Schematic Representation of the Processes Within the TCA for Total Copper Measurement.

The TCA has the potential for adaptation for the measurement of total dissolved Cu or free Cu ion in the effluent. The main difference between total recoverable and dissolved recoverable Cu is the filtration of the effluent before its acidification. This filtration process could easily be adapted into the TCA by placing a filtering system before the acidification of the sample. Once the effluent is filtered, the measurement of Cu in the effluent would be identical for both total recoverable and dissolved Cu. However, as effluent discharge is regulated as the total recoverable Cu, setting up the TCA for dissolved Cu measurements was not studied in this demonstration. Similarly, free Cu ion is not regulated at this time; therefore, this kind of measurement was not included in this effort. Nevertheless, the TCA could be easily adapted for the measurement of free Cu ion in the effluent, or in the receiving body of water. Concentration of free Cu ion is dependent on ligands, suspended solids, pH, ionic strength (salinity), temperature, and other chemical and biological parameters in the water. As the content and characteristics of these parameters is affected by acidification and digestion, avoiding these processes will provide the Cu-ISE with the real matrix for the measurement of free Cu ion. The TCA is capable of being modified for this purpose; however, a simpler system should be able to provide the same measurement.

2.3 PREVIOUS TESTING OF TECHNOLOGY

The use of the Cu-ISE for $Cu(II)_{aq}$ measurements was initially supported by the Harbor Processes Program of the Office of Naval Research (ONR). The effort was a general development of electrochemical sensors for real-time measurements in marine environments. The results of the ONR project were directed at the project "Real-time Monitoring of Copper from Effluent Discharges," funded by the Pollution Abatement Ashore Program, Y0817, which supports 6.4-type research. A product of this project was the creation of a Cooperative Research and Development Agreement (CRADA) with Thermo-Orion, Inc., the world's largest producer of electrochemical sensors and instrumentation. This CRADA promoted the collaboration with Steve West, head of the Research and Development Department of Thermo-Orion, for development of the TCA.

A prototype TCA in the final phase of development was tested under laboratory conditions at SPAWAR Systems Center-San Diego (SSC-SD) before starting the demonstrations. This testing was done in laboratory-controlled conditions with mixtures of seawater and freshwater of known total Cu concentrations in order to create calibration curves for the instrument at different salinities. The concentration in the mixtures was measured by GFAA, and each point represented a single point or mixture (Figure 3). The calibration curves are most noticeably affected by salinity, with a change in initial potential at a different salinity; however, the slope of the curves remained essentially constant (Figure 3). Therefore, it is necessary to measure the salinity of the effluent in order to select the most appropriate calibration curve. Since there is a direct relationship between salinity and conductivity at constant temperature, this is done by the conductivity probe in the TCA. Once this was accomplished, the working range determined under these laboratory conditions was from about 10 $\mu g/L^{-1}$ to 40 $\mu g/L^{-1}$, and the detected concentration had a precision of $\pm$ 3 $\mu g/L^{-1}$ at the 30 $\mu g/L^{-1}$ Cu level (Figure 4).

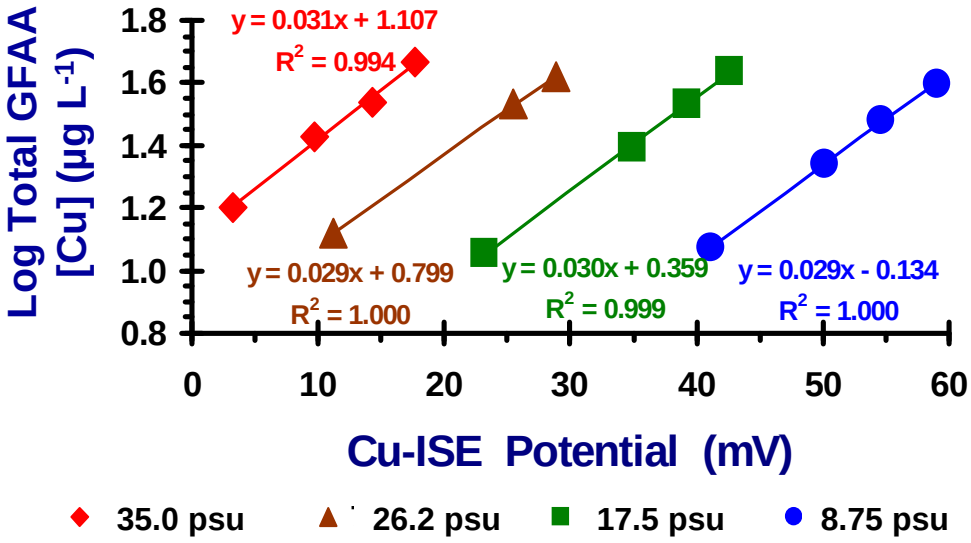

Figure 3. Calibration Curves at Different Salinities of the Potential (mV) Measured with the Jalpaite Cu-ISE in a Prototype TCA and the Total Copper Concentration Measured by GFAA.

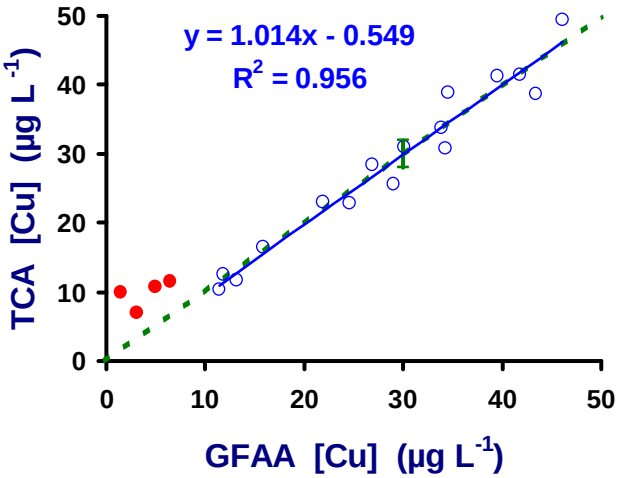

Figure 4. Comparison of Copper Concentrations Measured with the TCA with Those Measured by GFAA in a Suite of Mixtures of Seawater and Freshwater Under Laboratory Conditions. (The filled red circles are data not used for the regression. The green dashed line indicated the optimal response of 1:1.)

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The main advantage of the TCA is the capacity to measure total recoverable Cu in situ in near-real-time. Total recoverable Cu measured by the TCA is considered near-real-time, as there is a lag of 5 minutes from the time the effluent enters the TCA to the actual measurement. Despite this lag time, the TCA is able to continuously report total recoverable Cu in the effluent. For the demonstrations a reporting rate of 30 seconds, or 120 measurements per hour, was used; however, the rate of reporting can be adjusted with the computer down to every second, as desired. This is a great advantage over conventional procedures, which require sampling, shipping to commercial laboratories, and analysis, an expensive process with a turnaround period in the order of weeks.

A limitation of the TCA is the need for a reference electrode. As the potential is measured between the Cu-ISE and a reference electrode, the actual measurement is not absolute but relative, that is, the measured potential could vary when different reference electrodes are used. Therefore, it is of great importance to keep the characteristics of the reference electrode intact for the longest time interval possible. In the case of the TCA this is done by using an industrial reference electrode with high volume of internal reference solution.

The TCA requires about a week for equilibration with the effluent and a separate measurement of the Cu concentration in the effluent by other means in order to calibrate the instrument. In the three sites for the demonstration, one week was needed for the TCA to reach baseline response. This lapse of time is needed to purge the TCA of any source of metal in order to measure the concentrations in the discharge.

The TCA can be calibrated online by injection of known volumes of a standardized solution or by comparison with total recoverable Cu measured in grab samples following standard procedures (i.e., GFAA or ICP-MS). The online calibration is done after the equilibration time

mentioned in the previous paragraph, and it is accomplished with a computer-controlled calibration pump and a standard of known Cu concentration. Once the signal in the TCA is stable, the standard is pumped at three different flow rates, each one adding a specific amount of Cu to the sample. This information is used in conjunction with the measured Cu concentration to create a standard additions calibration of the Cu concentration in the sample.

A continuous source of effluent is required by the TCA. As the TCA continuously pumps effluent throughout its system, a volume of effluent is always required for its operation. The sites tested presented no problem with respect to this requirement; however, some effluents are sporadic and cannot fulfill this requirement. This could be overcome with the use of a recirculation system but was not addressed in this demonstration.

The TCA is affected by extreme changes in temperature. Initial laboratory studies indicated that the TCA is only affected when the ambient temperature of the location of the TCA was below 23°C. However, the demonstration at SBWWTP showed that extreme range in temperatures, even above 23°C, could affect the response of the instrument. Therefore, another limitation of this technology is the requirement of infrastructure with fairly constant temperature (i.e., a room or site not affected by large changes in temperature).

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3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The performance objectives for this demonstration are shown in Table 1. These objectives are based on performance and maintenance/operation of the TCA. They are designed to provide enough sensitivity and dynamic range for the use of the TCA in industrial settings, with regulatory requirements for Cu on the order of few parts-per-billion ($\mu g/L^{-1}$).

Table 1. Performance Objectives for the Demonstration of the TCA in Industrial Situations at PSNS, PHNS, and SBWWTP.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
Quantitative	Evaluate limit of detection	≤10 $\mu g/L^{-1}$ Cu	Yes
	Evaluate working range of TCA	10 to 50 $\mu g/L^{-1}$ Cu	Yes
	Evaluate precision of Cu measurement	± 10% at 30 $\mu g/L^{-1}$ level	Yes
	Evaluate reliability of measurements	±15% within working range	No
	Cost of operation	<$3K per year	No
Qualitative	Evaluate factors affecting TCA performance	Quantitative criteria at different salinities	Yes
	Evaluate reliability of TCA	Maintenance at monthly interval	No

3.2 SELECTION OF TEST SITES/FACILITIES

The main criterion used for the selection of demonstration sites was the need for continuous monitoring of total recoverable Cu concentrations in its discharges. Therefore, the selected sites are required by regulatory agencies for monitoring and controlling Cu in their discharges. This is the case with the dry docks at PSNS where, as mentioned above, a NPDES permit allows a daily maximum limit of total recoverable Cu of 33 $\mu g/L^{-1}$, with a monthly average of 19 $\mu g/L^{-1}$. In the case of the dry docks at PHNS a recently established interim NPDES permit allows a daily maximum limit of total recoverable Cu of 23 $\mu g/L^{-1}$.

The effluent at SBWWTP was selected in compliance with the Environmental Security Technology Certification Program (ESTCP) requirement to include a DoD non-Navy site. Several locations were considered for demonstration, and SBWWTP fulfilled the two main criteria for the demonstration, which were public concern of Cu loading and continuous discharge of freshwater effluent. Operators of the SBWWTP have interest in the fate of Cu through the treatment process and are interested in finding out the sources of Cu through this process.

The complexity in the industrial setting at the dry docks was expected to provide a range and variation in the Cu concentrations of their discharges. The results from the demonstration

indicate that the discharges at PHNS presented some variation and a larger range in concentrations, while those at PSNS were very stable regarding Cu concentration. Similar results to those from PSNS were observed at SBWWTP, where the Cu concentration remained stable.

The dry docks at PSNS and PHNS have good infrastructure for the deployment of the TCA. In both cases, the TCA was deployed in the Pump Well, a six-story deep subterranean structure at the side of the dry dock with pumping and controls for water and electrical systems. This structure is isolated from the outdoor environment and remains at fairly constant conditions of temperature and humidity; therefore, the temperate conditions in the Pump Well allowed for more stable response by the TCA. They also have access to a continuous source of effluent, in the case of PSNS, a mixture of seawater from the adjacent Sinclair Inlet and the effluent and, in the case of PHNS, as effluent in the sump at the bottom of the dry dock.

In contrast to the dry docks, where the TCA was under constant temperature and humidity, the location chosen for the placement of the TCA (i.e., a plastic hut located outdoors) at SBWWTP resulted in exposure to an extreme range in temperature throughout the day. This extreme range of temperatures affected the response of the instrument and influenced including the temperature-effect limitation for the use of the TCA.

3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

Three DoD sites were selected for the demonstration of the TCA—the dry docks at PSNS and PHNS, and the wastewater treatment plant at Schofield Barracks. PSNS is located adjacent to the City of Bremerton in western Washington, was established in 1891, is the Pacific Northwest's largest naval shore facility, and is one of Washington's largest industrial installations. The shipyard and the adjacent Naval Base Bremerton encompass 353 acres, 360 buildings, six dry docks, and nine piers with more than 2 miles of deep-water space. Dry Dock 6 is the largest dry dock owned by the Navy. The current mission of PSNS is maintenance for ships Navy-wide, including overhaul, repair, recycling, and engineering design work. Additionally, PSNS serves as a home port for several ships.

As its name denotes, PHNS is located in Pearl Harbor on the island of Oahu, Hawaii. The shipyard was established in 1908 and is the largest repair facility in the Pacific. With the Intermediate Maintenance Facility, it forms the largest industrial complex in Hawaii. The command encompasses 300 acres of land, 158 buildings, four dry docks, and 34 piers. There are six outfalls for the four dry docks at PHNS. The mission of PHNS is to provide maintenance to submarines and surface craft, including modernization, inactivation, surface ship complex overhaul, voyage repairs, and Pacific Fleet support.

Schofield Barracks is the Army's largest installation outside the continental United States. It was established in 1908 to provide a base for the Army's mobile defense of the island of Oahu, Hawaii. It is located in the Schofield Plateau between the Waianae and Koolau Ranges, near the town of Wahiawa in central Oahu. With an area of 17,725 acres, it is surrounded by rain forest, and it is used for housing, training, and industrial operations. Schofield Barracks houses the 25th Infantry Division (Light) unit, the Army Garrison, Hawaii; the 703rd Military Intelligence Brigade; the 45th Corps Support Group (Forward); and the Hawaii National Guard. The base

had a large population of about 12,005 active duty personnel with 11,380 family members, along with 3,000 Guard, 1,273 Reserve, and 2,673 civilians. Housing offers 667 officer-family units, 4,687 enlisted-family units, 36 unaccompanied officer units, and 26 unaccompanied enlisted units. Temporary lodging is also available, offering 192 guest house units. Industrial operations involved maintenance, repair, painting, and degreasing.

3.4 PHYSICAL SETUP AND OPERATIONS

The activities at dry docks generate wastewater such as bilge water, storm water runoff, and industrial wastewater, subject to federal, state, and local regulatory requirements. The operation and handling of discharges in dry docks is very complex, as shown for PSNS in Figure 5. There is identical complexity at PHNS not shown here. In order to capture the conditions in the effluent to Sinclair Inlet, the TCA was set up at the exit of the process water pumps at PSNS and for Pearl Harbor in the output of the process water pump discharge in PHNS.

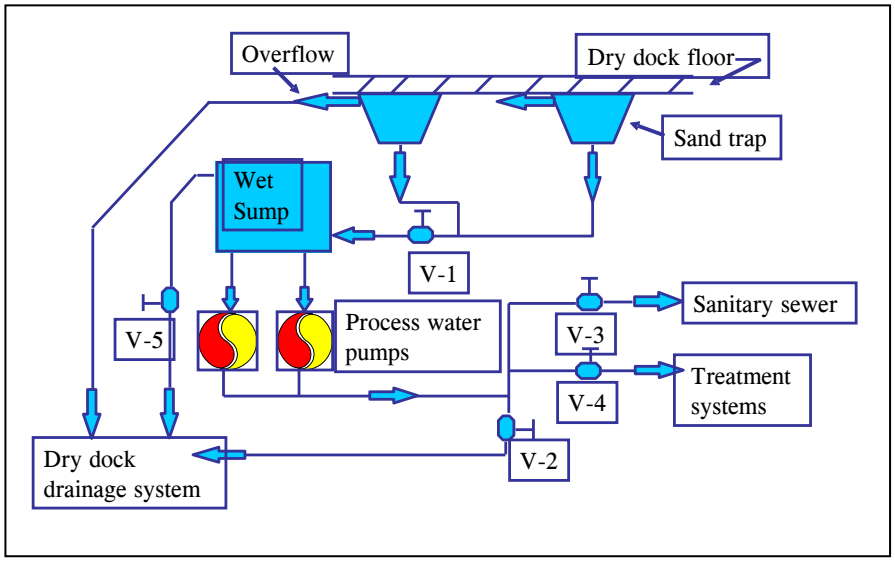

Figure 5. Diagram of Drainage Systems in a Dry Dock at PSNS.

In the case of PSNS, as stated above, an NPDES permit regulates the discharge of Cu to 33 $\mu g/L^{-1}$ from dry dock operations. In order to detect and avoid exceedances, the current approach is to collect discrete samples automatically and to send them for analysis in a laboratory. This provides an incomplete picture of the drainage system in the dry docks there. Furthermore, water discharges at PSNS are massive and complex, with a typical range of 4 to 10×10^{6} gal/day^{-1} in one discharge, made up of storm water, process water, seawater leakage, freeze protection water, and ship discharges. Therefore, without a real-time or near-real-time continuous monitoring at the process water pumps, the only option is treatment of the total discharge. In practice, the only water that requires treatment is that running off the dock floor, which is mostly from rain.

As indicated above, activities at PHNS generate wastewater such as bilge water, storm water runoff, and industrial wastewater, which are regulated via an interim NPDES permit for Cu to 23

$\mu g/L^{-1}$. Typical effluent discharge from the four dry docks in PHNS averages 3×10^{6} gal/day^{-1} (Earley et al., 2007).

The U.S. Army Directorate of Public Works, SBWWTP, provides secondary treatment for Helemano Military Reservation, Wheeler Army Airfield, Schofield Barracks, and Schofield Barracks East Range. The SBWWTP is a fully functional, stand-alone wastewater treatment facility that operates 24 hours per day, 365 days per year, with a typical influent flow of 2.4×10^{6} gal/day^{-1}. A schematic diagram of the treatment operations at SBWWTP is provided in Figure 6. The TCA was demonstrated in the effluent after the final sand filtration but prior to the chlorination step (not shown). This is done because the oxidative characteristics of bleach are known to affect the response of the Cu-ISE.

The treated effluent has relatively stable physical and chemical characteristics. Being a freshwater effluent, in comparison to the saltwater effluents where the TCA was demonstrated in the dry docks, the effluent at the SBWWTP did provide a different set of stable physical and chemical characteristics for the demonstration of the TCA. The sampling point for SBWWTP was after the final sand filtration (Figure 6).

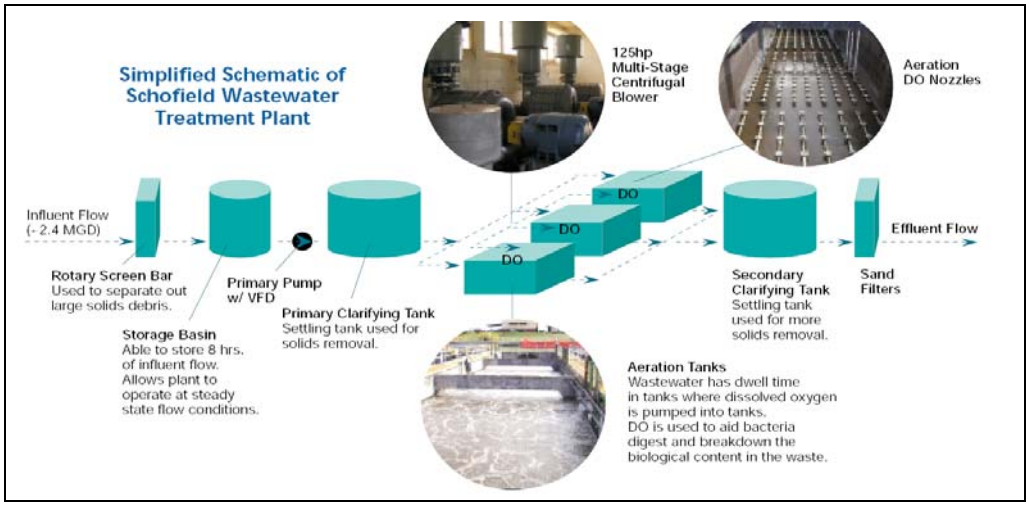

Figure 6. Diagram of the Treatment Process at SBWWTP. (The TCA was set in the effluent flow after the final sand filtration and prior to chlorination.)

3.5 SAMPLING AND MONITORING PROCEDURES

The main objective of the demonstration was to evaluate the precision and accuracy of the TCA to measure total recoverable Cu in the effluents from the dry docks at PSNS and PHNS, and from the treated effluent at SBWWTP, in situ and in near-real-time. This was achieved by comparing the concentrations measured by the TCA in the effluents with those measured by ICP-MS at Battelle and by GFAA at SSC-SD in grab samples from the same effluents. The analytical techniques used at these laboratories are listed in Rivera-Duarte et al. (2006), Appendix A. These techniques are the standard methods recommended by EPA. The experimental design consisted on continuously running the TCA and recording the output at 30-second intervals, providing a total of 120 measurements per hour, while systematically collecting discrete samples

for measurement at Battelle and SSC-SD. The collection of samples was done on the second week and the final weeks of each deployment. The sampling consisted of collecting duplicate grab samples (including all quality assurance/quality control [QA/QC] duplicate, blank, and split samples) every 8 hours, until a total of nine set of samples were collected each week. The samples from the last week of demonstration were also used to examine any performance degradation at the end of the 30-day maintenance cycle. One set of the duplicate samples was sent for total recoverable Cu concentration measurements by ICP-MS at the Battelle Marine Sciences Laboratory in Sequim, Washington, and a second sample was sent for analysis by GFAA at the analytical laboratory at SSC-SD in San Diego, California. The agreement among the Cu concentrations measured with the TCA and these two laboratories provided the information needed to determine the precision of the TCA. The accuracy was evaluated from automatic calibrations, done by injection of standards at known flow rates.

A second objective of the project is to examine the cost of operating the TCA with a 30-day maintenance cycle. This objective was approached by recording all expenses, including consumables and operator time during the scheduled one-month demonstration at the three sites.

3.6 ANALYTICAL PROCEDURES

The discrete samples collected at the TCA were acidified to pH 2 and analyzed using the standard methods, ICP-MS and direct injection GFAA, as described in Rivera-Duarte et al. (2006).

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4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

The performance of the TCA was evaluated for both quantitative and qualitative factors, as shown in Table 2 (see also Rivera-Duarte et al., 2006). Quantitative factors include analytical determination of its limit of detection, precision, dynamic range, reliability of measurements, easy of use, and maintenance. Factors affecting the performance of the TCA were considered as qualitative.

Among the qualitative factors that affect the response of the TCA are the salinity of the water, the temperature of the housing for the TCA, and the complexity of the effluent. Effects of salinity were detected since the preliminary testing of the TCA (Figure 3), and were corrected for the demonstrations. While the net change in the potential measured by the Cu-ISE increases in concentration, it is not affected by salinity, meaning that the electrode will have the same increase in potential from a specific increase in Cu concentration (i.e., same slope in the response). An increase in salinity will result in an actual increase in potential (i.e., a change in the intercept). Extreme changes in temperature in the place where the TCA is located affect the response of the TCA. Placement of the TCA in a setting with fairly stable temperature conditions will improve its response, as was the case in the dry docks at PSNS and PHNS. But, that was not the case at SBWWTP, where there was a considerable daily change in temperature in the shack where the TCA was located. And total recoverable Cu concentrations measured in the treated wastewater effluent from SBWWTP were erratic, with a measured concentration range much larger than that measured in grab samples. The extreme range in concentrations measured by the TCA could also be due to the complexity of the treated water, with extreme plant growth, presence of organic matter, surfactants, strong organic ligands used in the food industry, residual chlorine, and other compounds of common industrial and household use, that can affect the response of the Cu-ISE.

Laboratory controlled experiments were used to determine the limit of detection, accuracy, precision, dynamic range, and reliability of the TCA. The TCA was connected to the 16 MΩ cm^{-1} deionized (DI) system at SSC-SD and allowed to equilibrate for a couple of weeks, then a series of 15 automatic calibrations quantified the accuracy and precision. These calibrations consisted of injecting a standard of known Cu concentration at specific flow rates to increase the concentration in the stream of DI by desired values of 10, 20, 30, and 40 $\mu g/L^{-1}$. The standard is supplied by the calibration pump in the TCA (Figure 1, item 7) to a connection located just before the acidified and digested effluent reaches the Cu-ISE. The automatic calibrations are indeed standard addition calibrations and indicate an accuracy of 99% with a precision better than ±3 $\mu g/L^{-1}$ (±6.8%) at the 30 $\mu g/L^{-1}$ level, which is within the expected performance for the TCA (Tables 2 and 3). Accuracy and precision at several levels of Cu concentration, including the 30 $\mu g/L^{-1}$ are shown in Table 3. The calculated concentrations indicate an accuracy between 93 to 106% with a precision better than ±10% for concentrations of 20, 30, and 40 $\mu g/L^{-1}$, and a precision of ±12.8% for 10 $\mu g/L^{-1}$ total recoverable Cu. The accuracy is presented as the recovery of the expected concentration, and the precision is given as one standard deviation of the estimated concentration. This fulfills the performance objective criteria (Table 2) of ±10% at a 30 $\mu g/L^{-1}$ concentration level.

Table 2. Performance Criteria and Confirmation Methods for the Demonstration of the TCA.

Performance Criteria	Expected Performance (pre demo)	Performance Confirmation Method	Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Factors affecting TCA performance	Salinity effects	Observations from operation of TCA	Yes
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Cost	<3k/yr	Cost calculation	No
Limit of detection	<10 $\mu g/L^{-1}$	Comparison with concentrations in discrete samples measured at Battelle and SSC-SD	Yes
Working range of concentrations	<10 $\mu g/L^{-1}$ to 50 $\mu g/L^{-1}$	Comparison with concentrations in discrete samples measured at Battelle and SSC-SD	Yes
Precision of measurement	±3 $\mu g/L^{-1}$ at 30 $\mu g/L^{-1}$ level	Comparison with concentrations in discrete samples measured at Battelle and SSC-SD	Yes
Reliability of the measurements	±15% within working range	Comparison with concentrations in discrete samples measured at Battelle and SSC-SD	No
SECONDARY CRITERIA (Performance Objectives) (Qualitative)			
Ease of use	One week training sufficient for operation	Experience from demonstration operations	Yes
Maintenance	Once a month	Experience from demonstration operations	No

The limit of detection and the dynamic range of response of the TCA were evaluated under laboratory conditions in DI, and in DI with 3.2% NaCl. The latter was done as an approximation to seawater at salinity of 32 psu. The dynamic range in DI is from 0.5 $\mu g/L^{-1}$ (-8.1 Log Cu) to 400 $\mu g/L^{-1}$ (-5.2 Log Cu; Figure 7), while that in 3.2% NaCl is 2 $\mu g/L^{-1}$ (-7.5 Log Cu) to 400 $\mu g/L^{-1}$ (Figure 8). Therefore, the limit of detection for the TCA is 0.5 $\mu g/L^{-1}$ in freshwater and 2 $\mu g/L^{-1}$ in seawater. In both cases, the response was still linear at 400 $\mu g/L^{-1}$, and no effort was undertaken to extend the study beyond this upper limit.

Table 3. Average and One Standard Deviation for Concentrations Estimated for 15 Automatic Calibrations in Deionized Water.

[Cu] added ($\mu g/L^{-1}$)	Cu-ISE Potential (E) (mV)		Estimated Total Recoverable Copper ($\mu g/L^{-1}$)		Accuracy (%)	Precision (±%)
	Average	Standard Deviation	Average	Standard Deviation		
10	95.9	1.37	10.6	1.3	106	12.8
20	101.8	0.78	18.5	1.3	93	6.5
30	106.7	0.73	29.8	2.1	99	6.8
40	110.2	0.85	41.7	3.3	104	8.3

The reliability of the TCA seems to be affected by other unidentified factors. This is inferred from the single concentration injections of 40 $\mu g/L^{-1}$ Cu performed May 27 to 29, 2005, under the conditions mentioned in the previous paragraph. The average and one standard deviation for the 23 single concentration injections were 37.5 ± 6.53 Cu $\mu g/L^{-1}$, which is 16.3% of the 40 $\mu g/L^{-1}$ Cu concentration injected. In this case, there is the suspicion that the calibration pump in the instrument was responsible for this result. However, the performance criterion on the reliability of ±15% within the working range was not met.

Performance of the TCA under industrial conditions was satisfactory. Demonstrations in the dry docks of both PSNS and PHNS were successful. As shown in Table 4, total recoverable Cu concentrations measured by the TCA are in average within ±18% of the concentrations measured by conventional methods in grab samples. In both shipyards, the TCA was able to detect changes in Cu concentration associated with operational processes. At PSNS, the TCA detected the quitting of the Process Water Collection System at 0700 the morning of July 29, and the TCA measured an increase in concentration that day (Figure 9). At PHNS, the TCA recorded an increase in concentration every time the water pumps were working in order to empty the sump (Figure 10). This information provided by the TCA allowed management to determine the effects of these operational changes in the effluent of the dry docks.

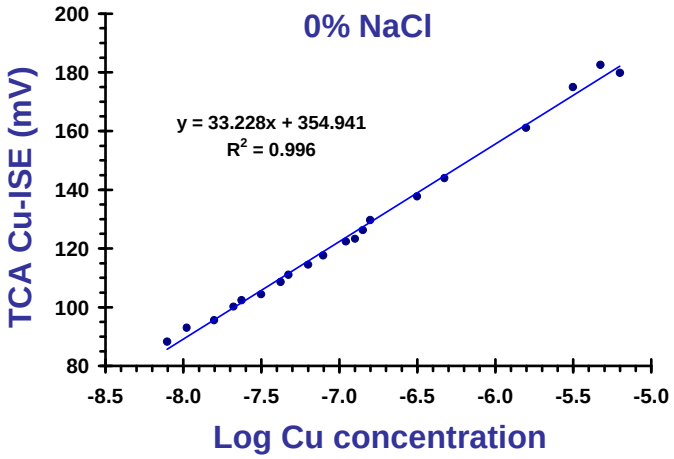

Figure 7. Dynamic Range of the TCA in DI. (The TCA had a linear response (R2 0.996) from a log of Cu concentration of -8.1 [0.5 $\mu g/L^{-1}$] to -5.2 [400 $\mu g/L^{-1}$]).

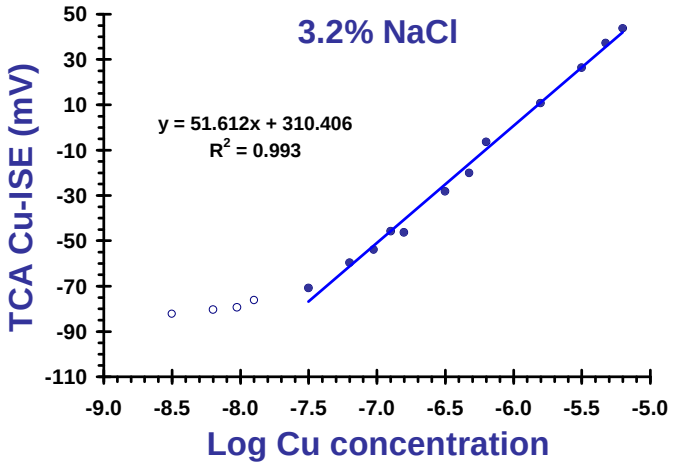

Figure 8. Dynamic Range of the TCA in Artificial Seawater (i.e., DI with 3.2% NaCl; salinity 32 psu). (The TCA had a linear response [R^2 0.993] from a log of Cu concentration of -7.5 [2 µg/L^{-1}] to -5.2 [400 µg/L^{-1}]).

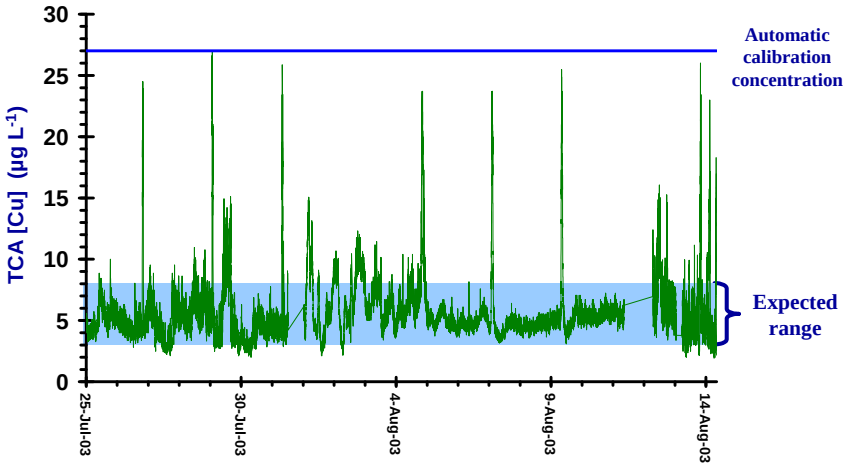

Figure 9. Total Recoverable Copper Concentrations (µg/L^{-1}) Measured by the TCA During the Demonstration at Dry Dock 6 of the PSNS.

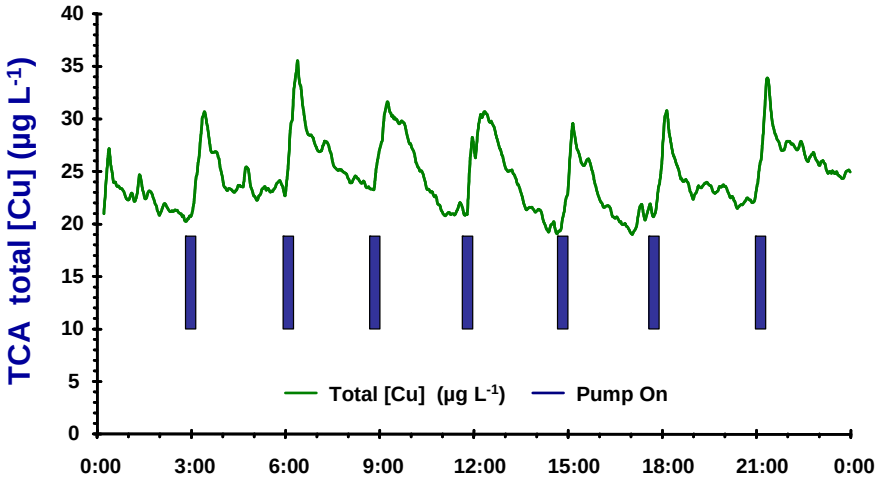

Figure 10. Response of the TCA to Pumping in Dry Dock 2 at PHNS. (An increase in total recoverable Cu was observed every time the pump was activated, and a subsequent decrease is observed once the pump is deactivated.)

4.2 PERFORMANCE CRITERIA

The performance of the TCA was assessed from measurements of samples following EPA accepted methodology. The performance factors were described in Section 4.1 and are shown in Table 2. Cu concentrations measured with the TCA were compared with Cu measurements done with conventional methods, GFAA at SSC-SD and ICP-MS at Battelle. Also, laboratory characterization was performed at SSC-SD, to evaluate some of these criteria. The performance of the TCA in measuring Cu concentrations in the effluent were estimated from the similitude among these analyses (Table 4).

Table 4. Comparison of the Total Recoverable Copper Concentrations ([Cu], µg/L^{-1}) Measured in Grab Samples from PSNS, PHNS, and SBWWTP at Battelle by ICP-MS and at SSC-SD by GFAA, with Those Measured in Real Time, In Situ by the TCA. (The differences are given by subtracting the measured value from that of the TCA.)

	Battelle [Cu] (µg/L^{-1})	SSC-SD [Cu] (µg/L^{-1})	TCA [Cu] (µg/L^{-1})	Difference Battelle [Cu] (µg/L^{-1})	Difference SSC-SD [Cu] (µg/L^{-1})	Difference Battelle [Cu] (%)	Difference SSC-SD [Cu] (%)
PSNS							
Average	4.37	4.6	5.2	0.84	0.66	18	14
Standard deviation	0.6	0.9	2.1	1.9	1.7	40	36
Maximum	5.70	7.2	10	5.1	4.2	104	82
Minimum	3.3	3.2	2.9	-2.0	-1.5	-39	-33
PHNS							
Average	32.8	30.4	32.8	-0.02	2.3	8	14
Standard deviation	7.8	6.1	10.9	13.7	13.6	53.5	54.2
Maximum	43.70	39.8	55.7	29.3	31.3	111	129
Minimum	17.30	18.5	22.5	-10.3	-11.5	-31	-34

Table 4. Comparison of the Total Recoverable Copper Concentrations ([Cu], µg/L^{-1}) Measured in Grab Samples from PSNS, PHNS, and SBWWTP at Battelle by ICP-MS and at SSC-SD by GFAA, with Those Measured in Real Time, In Situ by the TCA. (The differences are given by subtracting the measured value from that of the TCA.) (continued)

	Battelle [Cu] (µg/L^{-1})	SSC-SD [Cu] (µg/L^{-1})	TCA [Cu] (µg/L^{-1})	Difference Battelle [Cu] (µg/L^{-1})	Difference SSC-SD [Cu] (µg/L^{-1})	Difference Battelle [Cu] (%)	Difference SSC-SD [Cu] (%)
SBWWTP							
Average	5.19	4.5	13.1	7.9	8.6	155	194
Standard deviation	0.47	0.6	9.3	9.4	9.3	187	213
Maximum	6.06	5.6	33.2	28.3	29.0	584	697
Minimum	4.32	3.4	3.5	-1.9	-0.6	-35	-14

4.3 DATA ASSESSMENT

The main advantage of TCA over established procedures is the continuous measurement of the total recoverable Cu concentration in the effluent in real time in situ. The current approach for measurement of total recoverable Cu in effluents is collecting grab samples and analyzing them in off-site laboratories, a process that can take a couple of weeks. In comparison, the TCA provides continuous measurement of total recoverable Cu concentrations that can be modulated down to every few seconds as desired. This continuous measurement is termed near-real-time as there is a lag time of 5 minutes from sample introduction to the actual measurement by the TCA. The reliability of the TCA was confirmed by comparison to concentrations measured following the established methodology. The dynamic range and confidence of TCA measurements under industrial situations was evaluated by comparison with measurements in discrete samples analyzed at both Battelle and SSC-SD.

The dynamic range under industrial conditions is estimated by direct comparison of the range in concentrations measured at specific industrial sites. In this case, these are the effluents from the dry docks at PSNS and PHNS. The evaluation is based on direct comparison of the ranges in concentration measured by the three options (i.e., TCA, ICP-MS at Battelle, and GFAA at SSC-SD). While there was no statistical analysis of the significance of these comparisons, the confidence of the TCA-measured values supports these results and indicates a limit of detection of 8 µg/L^{-1} with a dynamic range to 80 µg/L^{-1} for the TCA under industrial conditions (data is not shown). In contrast, under controlled laboratory conditions, the response of the TCA was linear in a range from 0.5 to 400 µg/L^{-1} in DI and from 2 to 400 µg/L^{-1} in artificial seawater at salinity 32 psu (Section 4.1, Figures 7 and 8). All these ranges are considered relevant for industrial and regulatory purposes.

The confidence of the total recoverable Cu concentrations measured by the TCA was evaluated by correlating them with those measured at Battelle and SSC-SD. These correlations result in a slope and intercept that are then compared with the perfect correlation values of one and zero, respectively. As it was proved that there is no significant difference between the values measured under industrial conditions and the expected perfect values, then the Cu concentrations measured by the TCA are confident at the 95% level.

The precision of the TCA measurements can only be evaluated under controlled conditions. This is due to the large volume of water at constant concentration required for the TCA measurement. The precision was evaluated by performing a series of automatic calibrations in DI under laboratory conditions. For each automatic addition, a TCA concentration is used, and the average and standard deviation of all the automatic additions at the same level is evaluated. This evaluation indicates that the TCA has a precision better than ±10% of the expected value at 30 $\mu g/L^{-1}$. This is better than ±3 $\mu g/L^{-1}$ at this level.

The TCA is a user-friendly instrument; however, the user should have elemental knowledge in chemistry and the use of acids, computational software, and industrial settings. While this was not demonstrated, it should take about a week to learn to use the TCA. As the instrument requires an initial calibration at least a week after installation, hands-on experience could be provided at this time. Most of the problems encountered in these demonstrations are of simple mechanical origin and could be corrected by personnel with no experience in the use of the TCA. There are minimal health and safety requirements for the use of the TCA. The main safety use is regarding the preparation of the 5% nitric acid solution, which is of minimal safety concern once it is ready.

The main limitations to the use of the TCA are the complexity of the effluent and the temperature of the housing for the TCA. Performance of the TCA in the treated waste water effluent from SBWWTP was affected by the complexity of the effluent. However, the TCA performance was acceptable at the relatively simple effluents from the dry docks. Also, the TCA requires a setting with fairly constant temperature for better performance.

4.4 TECHNOLOGY COMPARISON

The performance of the TCA is similar to that from EPA-approved methodology, as indicated in Table 2. The only criterion that was not accomplished is the reliability of the measurement. There were instances when the total recoverable Cu measured by the TCA was beyond the ±15% difference limit from the Cu concentration in the sample. These results prevent the use of the TCA for regulatory purposes, but the TCA was developed as a management tool and not intended for regulatory purposes. As such, the TCA is able to provide information that allows the management of the effluent as a function of industrial operations.

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5.0 COST ASSESSMENT

5.1 COST REPORTING

Costs are reported following the Environmental Cost Analysis Methodology (ECAM) developed by the National Defense Center for Environmental Excellence (NDCEE, 1999). However, the ECAM analysis is performed only to level II, as many costs incurred for the demonstration and normal operation of the TCA are very difficult to distinguish from the costs of operating this prototype. Table 5 shows the costs that were tracked down for the commercial analysis of discrete samples (i.e., the current approach for measuring total recoverable Cu in effluents) following a monthly regulatory requirement. The costs associated with daily sampling and analysis of grab samples to approximate the information generated by the TCA are shown in Table 6. The costs associated with the use of the TCA (i.e., an instrument able to measure total recoverable Cu in situ in near-real-time at DoD-relevant concentrations) assuming a 10 year working-life are shown in Table 7. The comparison of these three types of costs provides an approximation of the potential benefits of the TCA.

Table 5. Costs Associated with Commercial Analysis of Discrete Samples for Total Recoverable Copper over 10 Years (at a rate of one sample per month as regulatory requirement).

Direct Environmental Activity Process Costs				**Indirect Environmental Activity Costs**		**Other Costs**	
Start-Up		**Operation and Maintenance**					
Activity	**$K[1]**	**Activity**	**$K**	**Activity**	**$K**	**Activity**	**$K**
Initial contracting	4.9	Labor to sample discharge	8.7	Test/analyze waste streams	3.6		
Sampling equipment purchase, including shipping and handling (S&H)	1.0	Consumables and supplies	0.4	Document maintenance	16.5		
Sampling site preparation	10.0	Equipment maintenance	0.1				
Training of sampling personnel	8.7						
TOTAL	24.6		9.3		20.1		
GRAND TOTAL	**54.0**						

[1] Costs are in thousands of U.S. dollars ($K)

Table 6. Costs Associated with Commercial Analysis of Discrete Samples for Total Recoverable Copper over 10 Years (at a rate of one sample per day for comparison to TCA output capability).

Direct Environmental Activity Process Costs				Indirect Environmental Activity Costs		Other Costs	
Start-Up		Operation and Maintenance					
Activity	**$K**	**Activity**	**$K**	**Activity**	**$K**	**Activity**	**$K**
Initial Contracting	4.9	Labor to sample discharge	264.9	Test/analyze waste streams	109.5		
Sampling equipment purchase, including S&H	1.0	Consumables and supplies	12.8	Document maintenance	16.5		
Sampling site preparation	10.0	Equipment maintenance	1.4				
Training of sampling personnel	8.7						
TOTAL	24.6		279.1		126.0		
GRAND TOTAL	**429.7**						

The TCA is not intended to mitigate costs associated with regulatory enforcement. These costs will remain in place as the TCA is a tool for discharge management, not a regulatory instrument. Therefore, the costs associated with the requirement of monthly sampling and analyses of the discharge (Table 5) will remain in place with the use of the TCA. The advantage of using a TCA is the optimization in managing the discharge provided by near-real-time measurements. This optimization includes better determination of the amount of effluent that requires treatment. For example, the average discharge from the dock floor at PSNS is less than 50,000 gallons day^{-1}, which, at a treatment cost of \$0.005 $gallon^{-1}$ could add up to \$91,250 $year^{-1}$, but this cost could be reduced by better detection and separation between an effluent that requires treatment and one that is compliant. Improving the management of the discharge could result in a better regulatory record by detecting and preventing processes that result in noncompliance. This type of cost associated with the use of the TCA is difficult or impossible to evaluate.

Table 7. Costs Associated with the TCA over a 10-Year Life Span. (Note that the costs associated with monthly discrete analysis of samples in a laboratory [Table 5] should be included here.)

Direct Environmental Activity Process Costs				Indirect Environmental Activity Costs		Other Costs	
Start-Up		Operation and Maintenance					
Activity	**$K**	**Activity**	**$K**	**Activity**	**$K**	**Activity**	**$K**
Equipment purchase	25.0	Labor to operate TCA	111.5	Document maintenance	16.5	Decommissioning	0.6
Equipment design	9.7	Utilities	1.1	Environmental Management Plan development and maintenance	16.6	Disposal of hazardous waste	1.2
Mobilization	2.0	Management/ treatment of by-products	2.4				
Site preparation	10.0	Consumables and supplies	4.3				
Installation	6.2	Equipment maintenance	5.7				
Training of operators	3.1	Training of operators	1.6				
TOTAL	56.0		126.6		33.1		1.8
GRAND TOTAL	**217.5**						

The TCA will provide continuous reporting of total recoverable Cu concentration throughout its working life. This type of reporting is not required for regulatory purposes but is important for discharge management. An approximation of costs associated with the continuous reporting provided by the TCA is shown in Table 6 as the costs for daily sampling and analysis of the effluent. Daily sampling will not provide the information supplied by the TCA. For example, it will not be able to differentiate the effect of any process that occurs in less than 24 hours. And the price is double that of the TCA ($429,700 compared to $217,500, as shown in Table 7). The costs of daily sampling are 158% of those for monthly regulatory sampling (Table 5) and TCA (Table 7) and still do not provide information for management of the discharge for short-term (i.e., hours) industrial processes.

5.2 COST ANALYSIS

Cost Comparison. For purposes of this comparison, the alternative activity for the measurement of total recoverable Cu in effluents is the commercial analysis of discrete samples. The TCA is not intended to be used in place of discrete samples for regulatory purposes, rather for situations where continuous control of Cu concentrations in near-real-time is required. For this cost analysis we have compared the cost of sampling once per day over a period of 10 years to the TCA's continuous measurement over the same 10-year period; however, this comparison is artificial. At best, a discrete sample would require a 1-2 hour delay in analysis, assuming the analytical equipment was located near the sampling point. In process control of dry-docks and wastewater treatment plant discharges, this delay would be unacceptable. Currently there is no commercial equipment capable of performing continuous total Cu measurements in real time.

Daily discrete sampling and off-site analysis results in approximately $429,700 for a 10-year effort. In comparison, use of the TCA in situ to provide continuous near-real-time measurement of total recoverable Cu is calculated to cost $217,500 for the same time period. The cost estimated for operation of the TCA for one year is approximately $20,000, considerably more than the expected $3,000 for performance objectives (Table 2) (Rivera-Duarte et al., 2006). However, the cost of the commercially available TCA is expected to be in the $25,000 range, and, assuming 10 years of working life, the annual cost of the TCA would be $25,000. This accounts for almost all of the $3,000 predicted.

In comparison to these costs, which are relatively easy to identify and quantify, there are costs that are very difficult to quantify, such as the advantage of having precise information on the concentration of total recoverable Cu in near-real-time. This type of information can be used to improve best management practices (BMP) as well as the optimization of the treatment of effluent waters.

In addition, cost avoidance is difficult to measure. Exceedances of Cu discharge levels could potentially result in fines and litigation. Since none of the demonstration sites has received a monetary fine or been sued by third parties for exceedances, these costs remain unknown.

Cost Basis. The anticipated costs bases that were used for cost analysis are the costs associated with operation and maintenance of the TCA, and the costs of sampling and analysis by a commercial laboratory (Tables 5 and 6).

Cost Drivers. The costs of operation and maintenance of the TCA will be driven by the supplies, training, and labor needed for these activities. The costs of the current approach of grab samples and off-site analysis are determined by a commercial contract and internal costs associated with sampling the discharge water.

Life-Cycle Costs. The costs estimated for the operation and maintenance of a TCA, assuming a lifetime of 10 years, are estimated from the demonstration test. These costs will include capital costs, such as purchasing, mobilizing, installing the TCA, operation, maintenance, and demobilization. The costs for installation include an initial period of three weeks for installation, equilibration, and calibration of the TCA. This is deemed necessary as a week for equilibration was required in the demonstrations.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

The estimated cost for operating the TCA for 10 years is approximately $217,500 (Table 7). This includes an approximate initial purchasing price of $25,000 and $126,500 in labor for operation and maintenance. In practice, some of these costs could be reduced by assigning these tasks to personnel responsible for management of the discharges.

The information provided by the TCA could result in significant savings. The TCA should support the improvement of BMP, optimizing the management of discharges, and decreasing or eliminating regulatory noncompliances. Savings from these activities are difficult to estimate, but they are an important factor that should be considered in the use of the TCA.

6.2 PERFORMANCE OBSERVATIONS

The performance by the TCA was within the performance criteria shown in Table 2. The only criterion that was not accomplished is the reliability of the measurement, which seems to be affected by other unidentified factors. This is inferred from the single concentration injections of 40 $\mu g/L^{-1}$ Cu performed May 27 to 29, 2005, which had a precision of ±16%. The average and one standard deviation for the 23 single concentration injections were 37.5 ± 6.53 Cu $\mu g/L^{-1}$, which is 16.3% of the 40 $\mu g/L^{-1}$ Cu concentration injected. In this case, there is the suspicion that the calibration pump in the instrument was responsible for this result. These results prevent the use of the TCA for regulatory purposes. The TCA was developed as a management tool, and it was not intended for regulatory purposes. As such, the TCA is able to provide information that allows the management of the effluent as a function of industrial operations.

The TCA is a user-friendly instrument; however, the user should have elemental knowledge in chemistry and the use of acids, computational software, and industrial settings. While this was not demonstrated, it should take about a week to learn to use the TCA. Since the instrument requires an initial calibration at least a week after installation, hands-on experience could be provided at this time. Most of the problems encountered in these demonstrations are of simple mechanical origin and could be corrected by personnel with no experience in the use of the TCA. There are minimal health and safety requirements for the use of the TCA. The main safety use is regarding the preparation of the 5% nitric acid solution, which is of minimal safety concern once it is ready.

The main limitations to the use of the TCA are the complexity of the effluent and the temperature of the housing for the TCA. Performance of the TCA in the treated waste water effluent from SBWWTP was affected by the complexity of the effluent. However, the TCA performance was acceptable at the relatively simple effluents from the dry docks. Also, the TCA requires a setting with fairly constant temperature for better performance.

6.3 SCALE-UP

This demonstration was run at full-scale implementation.

6.4 OTHER SIGNIFICANT OBSERVATIONS

None

6.5 LESSONS LEARNED

Temperature and salinity stability are important factors in operating the TCA. Controlling temperature can be accomplished by housing the TCA indoors in a location with minimal temperature swings. Salinity variations were shown to be a problem in the laboratory but were not encountered in the demonstration; however, the salinity concentration will affect the performance. End users should understand the laboratory salinity results before installing the TCA.

Most of the problems encountered with the TCA were related to simple mechanical functioning—plug-ups of sampling tubing, algae growth in sampling tubing, and excess particles in the tubing. On one occasion, the tubing was above the level of the acid and the head of the pump protruded. These problems were resolved with very simple mechanical solutions. Therefore, recognition and solving of malfunctioning warrants daily inspection to ensure smooth functioning of the TCA. This is a requirement that was not expected.

6.6 END-USER ISSUES

The capacity for real-time, in situ measurement of total recoverable Cu makes commercialization of the TCA an enterprise with great potential for success. The TCA could be used for management in many types of industrial settings, and its potential for reducing and/or eliminating regulatory liability makes it an asset for the industry. Similar concerns are in place in many DoD installations that have to comply with regulatory laws. TCA's potential to be a commercial success is supported by this need.

The characteristics of the effluent are the main factor in using a TCA. As the demonstration at SBWWTP showed, the TCA is prone to erratic response in a situation with large temperature variation and of complex mixture in the effluent. In general, any effluent with excessive organic matter load, with minimal content of bleach, chromium VI, or other oxidizing solution, or with changing concentrations of organic ligands, will not be suitable for total Cu measurement by the TCA. However, there is the potential for modification of the TCA for specific effluents. Another limitation of the TCA is that it requires daily maintenance and check-up. A minimum requirement is checking the instrument at least once a day for about a half hour to make sure it is functioning properly.

The TCA used for this demonstration is a custom built prototype. As shown in Figure 1, it consists of three boxes, each about 3×4×1 ft. The prototype TCA used for this demonstration was designed and built at SSC-SD and already includes several modifications recommended by Thermo-Orion Inc., the world's largest producer of electrochemical sensors and instrumentations. However, further modifications and downsizing are expected before the TCA is produced commercially by Thermo-Orion. A CRADA is in place for transferring the technology to Thermo-Orion.

6.7 APPROACH TO REGULATORY SUSTAINABLE INFRASTRUCTURE AND ACCEPTANCE

The application of the TCA for measuring total recoverable Cu concentrations has not been made known to regulators. However, once the capabilities of the TCA are demonstrated, its use and application will be made available to regulators and to the public through conferences and appropriate DoD information centers. The TCA was designed as a process-monitoring instrument, which will help in the optimization of the management of discharges. It is not intended to replace the periodic sampling required under most discharge permits. As such, regulator approval of the TCA is not required.

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APPENDIX A

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